Proceedings of the ASME 2020
International Mechanical Engineering Congress and Exposition
IMECE2020
November 16-19, 2020, Virtual, Online

IMECE2020-24217

CONDUCTIVE POLYMER-BASED SENSOR FOR SOIL NUTRIENT DETECTION

Yue He
Department of Mechanical Engineering, New York Institute of Technology
New York, NY

Shenglong Zhang
Department of Biological & Chemical Sciences, New York Institute of Technology
New York, NY

Ziqian Dong
Department of Electrical Engineering, New York Institute of Technology
New York, NY

Fang Li*
Department of Mechanical Engineering, New York Institute of Technology
New York, NY

ABSTRACT

To increase the production of crops, chemical fertilizers are used in crop fields. However, underuse or overuse cannot increase crop yields but even decrease them and cause severe environmental problems. Thus, the detection and monitoring of chemical concentration are increasingly important. To build up and monitor a data-based system for a large area, such a method is costly and time-consuming. In this research, we developed a conductive polymer-based sensor to detect nitrate concentrations in soil water. Conducting polymer poly(3,4-ethylenedioxythiophene)(PEDOT) was used as our sensing material. To increase its conductivity, we used the vacuum phase polymerization method to achieve a high conductive and stable polymer film. The conductivity of the polymer film is 500 S/cm. Our results have demonstrated that the conductive polymer-based sensors have high sensitivity to nitrate solution. The response to 1000 ppm nitrate solution is 47.2% (Response = $(I_{nitrate} - I_{DIwate}) / I_{DIwater}$*). The sensors can detect nitrate range from 1ppm to 1000 ppm. The response time is less than 1 minute. This impedance-based sensor will eventually be integrated with the surface acoustic wave sensors, combined with an antenna and a GPR unit for low maintenance, autonomous, and in-situ soil nutrient sensing.*

Keywords: Conducting polymers, Soil sensors

1. INTRODUCTION

Nowadays, Human activities, chemical agriculture over-use, and climate changes show threats to soil fertilization. The changing condition of soil has a great influence on human development. The monitor system for soil physical conditions needed for modern agriculture. Current technique to measure soil properties relies on taking samples from place to place and takes them for laboratory testing [1]. To build up and monitor a data-based system for a large area, such a method is costly and time-consuming. To meet the high demand of next-generation soil monitoring devices, scientists are developing new materials for sensor applications. These sensors are used in environment control, field status diagnostics, and so on. Sensors should have basic characteristics and improved performance, such as low cost, high response, fast response/recovery time, both short- and long-term stability, compact in size, and low power consumption.

In this research, we developed a conductive polymer-based(Poly(3,4-ethylenedioxythiophene) (PEDOT)) sensor to detect nitrate concentrations in soil water. PEDOT is one of the most conductive and stable conducting polymers. The applications of PEDOT is vast. For examples, PEDOT is used in biosensors[2], Organic Light Emitting Diodes (OLED)[3]. Other methods to obtain PEDOT such as chemical oxidation and electropolymerization have defects like low conductivity, poor stability, and solvent dependency [4]. In this research, vacuum phase polymerization (VPP) method was chosen for PEDOT synthesis as it [5] can achieve a high conductive and stable polymer film in water solution. Our results have shown that the polymer as prepared has high conductivity with 500 s/cm.. The response to 1000 ppm nitrate solution is 47.2% (Response = $(I_{nitrate} - I_{DIwate})/ I_{DIwater}$) The PEDOT-based sensors can detect nitrate range from 1ppm to 1000 ppm. The response time is less than 1 minute. This impedance-based sensor will eventually be integrated with the surface acoustic wave sensors, combined with an antenna and a GPR unit for low maintenance, autonomous, and in-situ soil nutrient sensing.

2. MATERIALS AND METHODS

2.1 Materials and equipment

Iron(III) p-toluenesulfonate hexahydrate, n-Btanol, 3,4-Ethylenedioxythiophene 97%(EDOT) monomer, and PEG-PPG-PEG, Mn=5800 were obtained from Sigma-Aldrich. Plain glass microscope slides (75mm x 25mm), IPA (Isopropyl Alcohol), acetone, ethanol and DI(Deionized) water obtained from Fisher Chemical. All chemicals were used as received. Equipment that we used includes a spin coater (Brewer Science), a hot plate (Brewer Science), a VWR 1490 vacuum oven (127 L), a plasma gun, the AJA ATC-Orion 8 UHV sputtering system, the Alpha-Step D-600 profiler, and the Keysight 2410 source meter.

2.2 Sensor fabrication and characterization

The PEDOT-based nitrate sensor, as shown in Figure 1 a), consists of a glass substrate, Gold electrodes, and VPP-synthesized PEDOT thin film. To fabricate the sensors, first, glass slides were washed with acetone, IPA and DI water and dried by nitrogen spray. Before the sputtering process, the substrates were treated with plasma for 2 minutes. The substrates were covered by a shadow mask with electrode patterns and then a 150 nm gold film was deposited onto the substrates through the mask.

Once the electrodes were fabricated, a PEDOT film was synthesized via the VPP method. First, Iron(III) p-toluenesulfonate hexahydrate was dissolved in n-Butanol to produce a 21.3 wt% oxidant solution. After that, a working solution was prepared by adding 10 wt% PEG-PPG-PEG in 21.3 wt% Iron(III) p-toluenesulfonate oxidant solution. The working solution was then spin-coated on the substrates with electrodes at a speed of 1500 RPM for 25 seconds. To remove the solvent in the films, the samples were then baked on a hot plate at 70 ºC for 60 seconds. After baking, they were put into a vacuum oven with the temperature set as 35 ºC. The EDOT monomer was placed on a 45ºC hot spot inside the vacuum oven. The vacuum oven was pumped down to 45 mbar. An externally mounted small chamber with a valve and loaded with DI water was opened and let water vapor get in the oven. The polymerization time is 25 minutes. Then, the samples were rinsed with ethanol carefully to remove any un-reacted chemicals. The samples were then dried by air.

A tiny soft brush was used to scratch out the polymer above the gold electrodes and leave gold electrodes on the substrates. Then, polymer film around the electrodes scratched off to get desired patterns. Then used low cure temperature silver paste to bound wires to the electrodes. Figure 1 b) shows a sample after scratching the polymer surround electrodes.

To characterize the conductivity of the PEDOT film, we measured the thickness (h) of the polymer film with a stylus profiler (Alpha-Step D-600). To characterize the conductivity of the thin film, the resistance (R) between each pair of electrodes was measured by a source meter with the applied DC voltage of 0.2mV. The conductivity of the thin film was calculated with the following equation

$$\text{Conductivity}=\frac{W}{L*R*d} \qquad (1)$$

where W and L are the width and length of the thin film respectively, as shown in Figure 1 a).

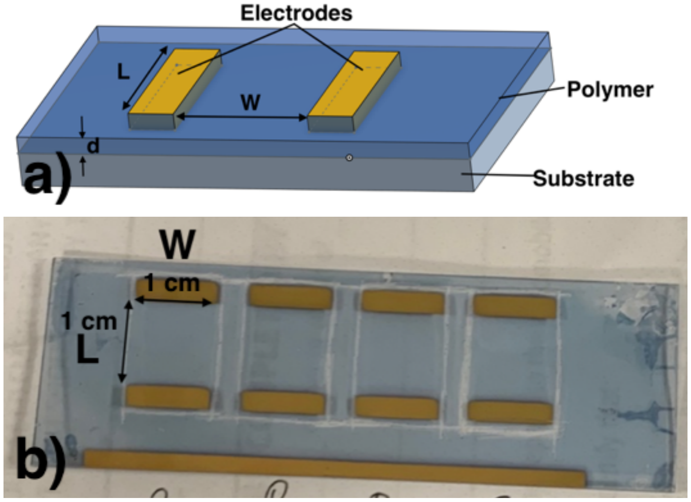

FIGURE 1: a): Layout of the soil sensor. The gold electrodes were on the substrate. b): Polymer samples that after scratching the polymer surrounding the electrodes. The transparent blue films are PEDOT polymer. The golden rectangular is the electrode terminal.

2.3 Sensing test

All the sensing tests were performed under the ambient condition. To test the sensors for nitrate sensing, sensors were connected to the source meter and kept in different concentrations of the nitrate solution. The source meter applied 0.2 mV DC voltage and the electrical resistance was recorded every 100 seconds. When not measuring the samples, the voltage was not applied.

The sensitivity and repeatability of the PEDOT-based sensors for nitrate sensing were tested. For the sensitivity test, sensors were exposed to nitrate solutions with concentrations of 1 ppm, 10 ppm, 100 ppm, and 1000 ppm respectively, and then from 1000 ppm nitrate to 100 ppm 10 ppm and 1 ppm nitrate respectively. For the repeatability test, sensors were dipped into DI water and then exposed to 100 ppm nitrate, and repeat the process.

3. RESULTS AND DISCUSSION

The PEDOT film was obtained after 25 minutes of polymerization. The thickness of the polymer film measured by the profiler is 150 ± 10 nm. We tested four samples. The conductivity was (500 ± 30 S/cm). Fabretto M and his team have synthesized over PEDOT film with the VPP method. They got a maximum conductivity of 1100 S/cm for their samples [6]. In our experiment, the thickness of the polymer was controlled by the spinning speed during the spin coating. The thicker the polymer film is, the longer the response and recovery time will be. On the other hand, if the polymer film is thinner than 100 nm, the surface of the film will be uneven after the polymerization process. Thus, we chose a 150 nm thick film to compromise film quality and response time.

Figure 2 shows the change in the resistance of the device with time when exposed to different concentrations of nitrate solutions. We could see that the resistance decreases when the sensor was exposed to the nitrate solutions with the concentrations from 1 ppm to 1000 ppm and the resistance increases with the concentrations decreases from 1000 ppm to 1 ppm. The change in the thin film resistance could be attributed to the fact that the thin film can absorb and release nitrate onions and this occurs without the application of an external electric potential. From the results, we have also observed that the response and recovery time are dependent on the concentration of the nitrate solution. The response time to the nitrate solution with the concentration of 1000 ppm is less than one minute while when the sensor is exposed to 1 ppm nitrate solution from 10 ppm nitrate solution, the resistance could not reach the final settled value after 10 mins.

Figure 3 shows the sensor response, which is defined as the ratio of resistance change after ion addition ($I_{nitrate}$ - I_{DIwate}) to the initial resistance when the device is exposed to DI water ($I_{DIwater}$), as functions of the concentrations of solutions in a logarithmic scale. The response to the 1000 ppm nitrate solution is 47.2%.

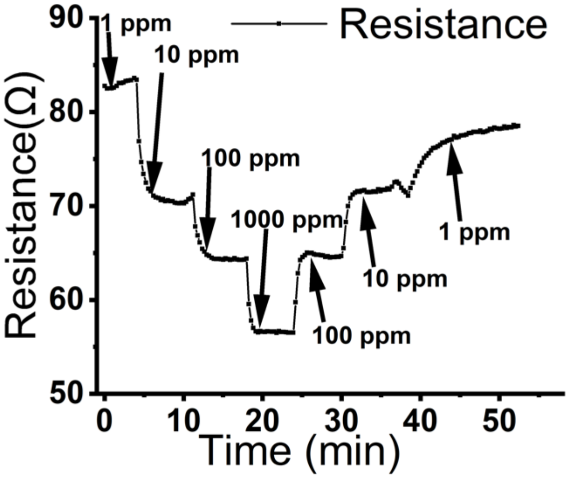

FIGURE 2: Relationship between the resistance of the sensor and the concentration of nitrate solution.

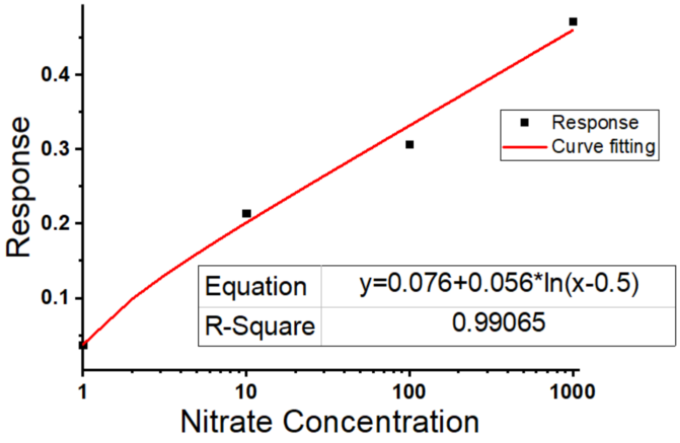

FIGURE 3: Relationship between the response and the concentration of nitrate solution.

Figure 4 shows the repeatability test results for 5 cycles. The device was alternatively exposed to DI water or a 100 ppm nitrate solution for 5 cycles. It has been shown that the variation in resistance with the device exposed to a 100 ppm solution for each cycle is 62.4 ± 1Ω. However, the repeatability test shows the difference between the response time and recovery time. The response time to a 100 ppm nitrate solution is about 2 minutes. The time for sensors to recover from a 100 ppm nitrate solution to DI water takes longer than 5 hours.

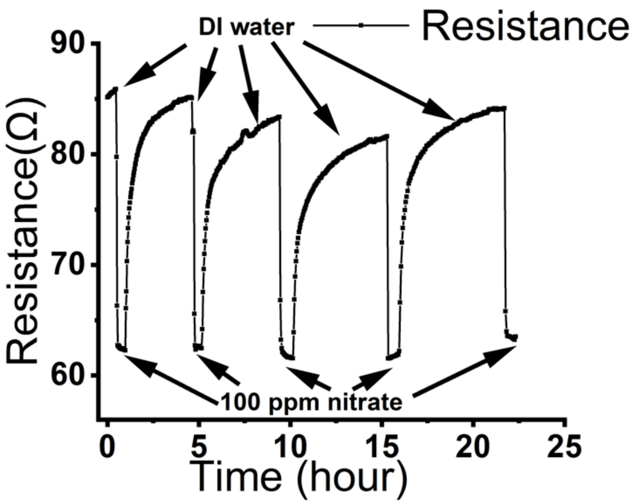

FIGURE 4: Resistance changes when doing the repeatability test. The samples were exposed to a 100 ppm nitrate solution and DI water for five cycles.

4. CONCLUSION

In this research, we used the vapor phase polymerization method to synthesize high conductive polymer-based low energy cost (<0.1 μ W) soil sensor with high sensitivity (47.2% to 1000 ppm nitrate) and stability. We are now doing experiment on the selectivity of our sensors. We are performing extra tests for other solution including sodium chloride and sodium sulfate solution. Also, we are combing those nutrient together and measuring the respond to nitrate with different combination of nutrients.

ACKNOWLEDGEMENTS

This material is based upon work supported by the National Science Foundation under Grant No. 1841558. The authors would like to thank Dr. Chang-Yong Nam from Brookhaven National Laboratory for his comments and suggestions for this research.

REFERENCES

[1] UNEP, UNCCD; GEO 5; Global Environmental Outlook; Managing Increasing Pressures on Land Retrieved October 20,

2015, http://www.unep.org/geo/pdfs/geo5/GEO-5_LAND-small.pdf
[2] Kros A, van Hövell SWFM, Sommerdijk NAJM, Nolte RJM. Poly(3,4 - ethylenedioxythiophene) - Based Glucose Biosensors,2001
[3] Kim WH, Mäkinen AJ, Nikolov N, Shashidhar R, Kim H, Kafafi ZH. Molecular organic light-emitting diodes using highly conducting polymers as anodes, 2002
[4] Michael Mueller, Manrico Fabretto, Drew Evans. Vacuum vapour phase polymerization of high conductivity PEDOT: Role of PEG-PPG-PEG, the origin of water, and choice of oxidant, 2012
[5] abretto M, Jariego-Moncunill C, Autere J-P, Michelmore A, Short RD. High conductivity PEDOT resulting from glycol/oxidant complex and glycol/polymer intercalation during vacuum vapour phase polymerization, 2011
[6] Fabretto M, Autere J-P. Vacuum vapour phase polymerised poly(3,4-ethyelendioxythiophene) thin films for use in large-scale electrochromic devices, 2011